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"Material comprising an organic UV-A screening agent and
process for shifting the maximum absorption wavelength"

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**MATERIAL COMPRISING AN ORGANIC UV-A SCREENING AGENT AND
PROCESS FOR SHIFTING THE MAXIMUM ABSORPTION WAVELENGTH**

5 The present invention generally relates to a
material obtained by the sol-gel route exhibiting a
maximum absorption wavelength (λ_{\max}) within the range from
370 to 400 nm, to a process for shifting the maximum
absorption wavelength of a material comprising an organic
UV-A sunscreen agent and to a cosmetic and/or
10 dermatological composition including such a material.

It is known that light radiation with wavelengths
of between 280 nm and 400 nm makes possible browning of
the human epidermis and that rays with wavelengths of
between 280 nm and 320 nm, known under the name of UV-B
15 radiation, result in erythemas and cutaneous burns which
can be harmful to the development of natural tanning;
this UV-B radiation therefore has to be screened out.

It is also known that UV-A rays with wavelengths
of between 320 and 400 nm, which result in browning of
the skin, are capable of bringing about a detrimental
change in the latter, in particular in the case of
sensitive skin or of skin continually exposed to solar
radiation. UV-A rays result in particular in a loss of
elasticity of the skin and the appearance of wrinkles,
20 leading to premature aging. They promote the triggering
of the erythematous reaction or enhance this reaction in
some subjects and can even be the cause of phototoxic or
photoallergic reactions. It is therefore desirable also
to screen out UV-A radiation.

30 The commonly used sunscreen agents do not include
organic screening agents effective in the long UV-A
spectral range corresponding to wavelengths ranging from
370 to 400 nm. In other words, antisun protection is not
provided in this spectral range. This is all the more
35 serious as this more penetrating radiation is partly
responsible for the development of certain skin cancers

and of immunosuppression, in addition to cutaneous photoaging.

In the state of the prior art, Patent Applications PCT numbers WO 93/10753 and WO 93/11135 of Slavtcheff et al. respectively disclose a sunscreen agent of metal complex of dibenzoylmethane derivatives type, the maximum absorption wavelength of which is 366 nm, and a process for the preparation of this novel sunscreen agent. Currently, appropriate organic UV-A sunscreen agents exhibiting a maximum absorption wavelength (λ_{\max}) of greater than or equal to 370 nm with a coefficient of extinction $\epsilon > 25\ 000\ \text{mol}^{-1}.\text{l}^{-1}.\text{cm}^{-1}$, preferably $\epsilon > 30\ 000\ \text{mol}^{-1}.\text{l}^{-1}.\text{cm}^{-1}$, are unknown.

It has been found, surprisingly, that, by combining an organic UV-A screening agent having a maximum absorption wavelength (λ_{\max}) of less than 370 nm, such as 4-tert-butyl-4'-methoxydibenzoylmethane (Parsol® 1789; $\lambda_{\max} = 358\ \text{nm}$), with certain zirconium, titanium and aluminum compounds, it is possible to obtain a material for which the absorption band is shifted and which exhibits a maximum absorption wavelength within the range from 370 to 400 nm, with an ϵ value which is not significantly reduced.

A subject matter of the present invention is therefore a material capable of being obtained by the sol-gel route comprising at least one organic UV-A sunscreen agent with a λ_{\max} of less than 370 nm and at least one zirconium, titanium or aluminum compound, the material having a maximum absorption wavelength which is situated in the range from 370 to 400 nm.

The present invention also relates to a process for shifting the maximum absorption wavelength of an organic UV-A sunscreen agent with a λ_{\max} of less than 370 nm into the range from 370 to 400 nm.

A further subject matter of the present invention is cosmetic and/or dermatological compositions for the

photoprotection of the skin and/or keratinous substances comprising a material of the invention.

Other characteristics, aspects and advantages of the invention will become more clearly apparent on reading the description and examples which follow.

A subject matter of the present invention is a material capable of being obtained by the sol-gel route which exhibits a maximum absorption wavelength (λ_{\max}) within the range from 370 to 400 nm and which comprises:

(a) at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides,

(b) at least one organic UV-A sunscreen agent, the maximum absorption wavelength of which is less than 370 nm,

(c) at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer,

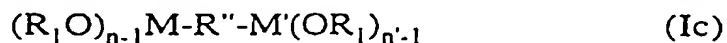
(d) at least one solvent, and

(e) an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation.

The term "organic UV-A sunscreen agent" is understood to mean any organic compound which absorbs UV radiation within the 320-400 nm wavelength range.

The metal alkoxides are chosen from the group composed of:

(1) metalloorganic compounds corresponding to one of the following formulae:



in which:

M and M' represent, independently of one another, a zirconium, titanium or aluminum atom,

n and n' denote the respective valencies of the metal atoms represented by M and M',

5 R₁ represents a saturated or unsaturated and linear or branched C₁₋₃₀, preferably C₁₋₆, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, sulfur, oxygen or phosphorus atom, and more preferably a linear or branched C₁₋₃₀, preferably C₁₋₆, alkyl group,

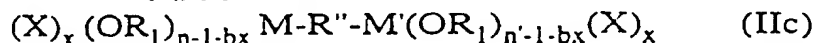
10 R and R' represent, independently of one another, a saturated or unsaturated and linear, branched or cyclic C₁₋₃₀, preferably C₂₋₂₀, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or
15 branched alkyl group, a cycloalkyl group or an aryl group,

it being possible for said R and R' groups to be substituted by groups capable of reacting with the functionalized organic or silicone polymer, such as, for
20 example, halogen atoms, the hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino or pyrrolo groups, groups comprising ethylenic unsaturation, such as the (meth)acrylic and vinyl groups,
25 halogenated groups, such as perfluorinated groups, hydroxylated or carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate
30 (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives, and the like, and it being possible for said R and R' groups to additionally comprise a cosmetically or dermatologically active group chosen, for example, from a colorant group, a
35 photochromic group, a group for screening out UV radiation, a group for promoting adhesion to keratinous

substances (such as groups of amide, urethane, urea, hydroxyl, carboxyl, amino acid or polypeptide type), a group for facilitating the removal of makeup, a bactericidal group, a chelating group which can in particular complex polyvalent cations, a hydroxy acid, a neurosuppressant, a group for combating hair loss, an antioxidizing group, a group for combating free radicals or a vitamin-carrying group,

R'' represents a saturated or unsaturated and linear, branched or cyclic divalent C₁₋₃₀, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or branched alkylene group, a cycloalkylene group or an arylene group, it being possible for said R'' group to be substituted by groups capable of reacting with the organic or silicone polymer, such as those defined above, and it being possible for said R'' group additionally to comprise a cosmetically or dermatologically active group, such as those defined above;

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



in which:

M, M', n, n', R₁, R, R' and R'' have the same meanings as those given for the above formulae (Ia) to (Id),

X represents a monodentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic polymer or said functionalized silicone polymer (c), such as, for example, those defined above, and which

can comprise a cosmetically or dermatologically active group, such as, for example, those defined above, x represents the number of X ligands; and b represents the number of bonding atoms of the X ligand.

5 The term "monodentate ligand" is understood to mean a group comprising a single atom which can bond to the central metal atom.

10 The term "chelating group" is understood to mean a polydentate ligand bonded to a single central metal atom by more than one doublet-donating atom.

15 Mention may be made, as examples of such monodentate or polydentate ligands (X), of sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones, β -diketones, esters, β -ketoesters, amines, β -ketoamines, amino acids, preferably α - or β -hydroxylated amino acids, and their derivatives, α - or β -hydroxy acids, ethers and polyethers, imines, optionally hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, 20 optionally cyclic thioethers, di(thioethers), monoalcohols or polyols, dextrin and its derivatives, or thiazolidines.

25 Mention may in particular be made of diketones, such as 2,4-pentanedione, 2,4-hexafluoropentanedione or 2,2,6,6-tetramethyl-3,5-heptanedione; salicylic acid and its derivatives, such as 4- or 5-((meth)acrylamino)salicylic [sic] acid; lactic, succinic, acetic and citric acid; (meth)acrylic acid esters, such as acetoxyethyl methacrylate or methyl α -hydroxy(meth)acrylate; ethyl acetoacetate, methyl 30 acetoacetate and acetylacetone; EDTA; polyethers of low molecular mass, such as poly(ethylene glycol)s and poly(propylene glycol)s; polyethyleneimines; lysine and its derivatives, such as ϵ -N-(meth)acryloyl-L-lysine; 35 cysteine and its derivatives, such as N-acetylcysteine, carboxymethylcysteine, cystine or N,N'-diacetylcystine;

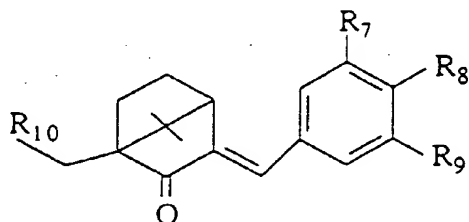
methionine; lactic acid esters or acetic acid esters; triethanolamine; lipoic acids; or dextrin or cyclodextrin.

5 Preference is very particularly given, among the metal alkoxides mentioned above, to tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

10 The organic UV-A sunscreen agent having a λ_{\max} of less than 370 nm can be any appropriate organic compound having a maximum absorption wavelength of less than 370 nm.

Mention may be made, among organic UV-A sunscreen agents which can be used according to the invention, of:

- 15 (1) dibenzoylmethane derivatives;
(2) screening agents active in the UV-A region of following formula (IV):



(IV)

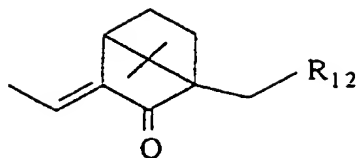
in which:

20 R₇ and R₉, which are identical or different, represent a hydrogen atom, a halogen atom, an OH group, a saturated or unsaturated and linear or branched C₁-C₁₀ alkyl group, a saturated or unsaturated and linear or branched C₁-C₁₀ alkoxy group or an HSO₃ group;

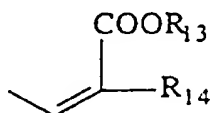
R₁₀ represents a hydrogen atom or HSO₃;

25 R₈ represents a hydroxyl group; an OR₁₁ group where R₁₁ represents a saturated or unsaturated and linear or branched C₁-C₁₀ alkyl group;

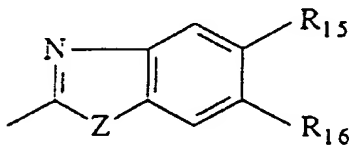
or else a group of following structure:



in which R_{12} represents a hydrogen atom or HSO_3 ;
or else a group of following formula:



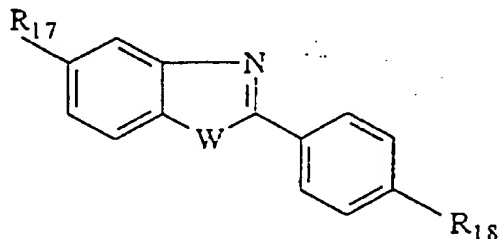
or else a a [sic] group of following formula:



in which:

5 Z represents an oxygen atom or an -NH- group;

R_{13} , R_{14} , R_{15} and R_{16} , which are identical or
different, represent a hydrogen atom, a halogen atom, an
OH group, a saturated or unsaturated and linear or
branched C_1 - C_{10} alkyl group; a saturated or unsaturated and
10 linear or branched C_1 - C_{10} alkoxy group; or an HSO_3 group;
(3) screening agents which are active in the UV-A region
of the benzimidazole or benzoxazole type of following
formula (V):



(V)

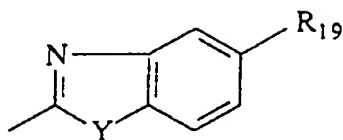
in which:

15 W represents an oxygen atom or an -NH- group;

R_{17} represents a hydrogen atom or HSO_3 ;

R_{18} represents a linear or branched alkoxy group
comprising from 1 to 10 carbon atoms approximately or a

group of following formula:

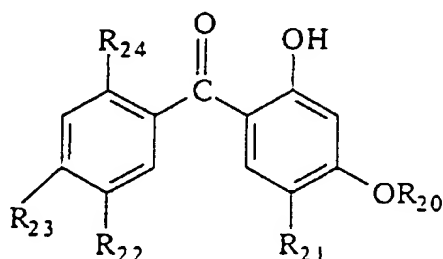


in which:

Y represents an oxygen atom or an -NH- group;

R₁₉ represents a hydrogen atom or HSO₃;

- 5 (4) benzophenone derivatives, such as those of following formula (VI):



(VI)

in which

R₂₀ represents a hydrogen atom or a saturated or unsaturated and linear or branched C₁-C₁₀ alkyl group;

- 10 R₂₁ and R₂₂, which are identical or different, represent a hydrogen atom, a halogen atom, an OH group, a saturated or unsaturated and linear or branched C₁-C₁₀ alkyl group; a saturated or unsaturated and linear or branched C₁-C₁₀ alkoxy group or an HSO₃ group;

- 15 R₂₃ represents a hydrogen atom, OH, a saturated or unsaturated and linear or branched C₁-C₁₀ alkyl group or a saturated or unsaturated and linear or branched C₁-C₁₀ alkoxy group;

- 20 R₂₄ represents OH, a hydrogen atom or a saturated or unsaturated and linear or branched C₁-C₁₀ alkyl group;
(5) silane derivatives or polyorganosiloxanes comprising benzophenone group(s), such as those disclosed in documents EP-A-0 389 377, FR-A-2 657 351 and EP-A-0 655 453;

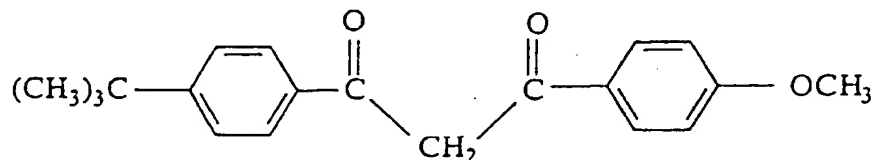
- 25 (6) anthranilates; and

(7) their mixtures.

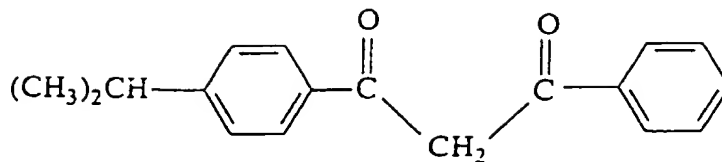
Mention may especially be made, among dibenzoylmethane derivatives which are particularly well suited in the context of the present invention, of, without implied limitation:

2-methyldibenzoylmethane,
4-methyldibenzoylmethane,
4-isopropyldibenzoylmethane,
4-tert-butyldibenzoylmethane,
2,4-dimethyldibenzoylmethane,
2,5-dimethyldibenzoylmethane,
4,4'-diisopropyldibenzoylmethane,
4,4'-dimethoxydibenzoylmethane,
4-tert-butyl-4'-methoxydibenzoylmethane,
2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,
2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane,
2,4-dimethyl-4'-methoxydibenzoylmethane,
2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

Preference is in particular given, among the dibenzoylmethane derivatives mentioned above, to 4-tert-butyl-4'-methoxydibenzoylmethane, sold in particular under the trade name of "Parsol[®] 1789" by Hoffmann-Laroche, this screening agent corresponding to the following expanded formula:



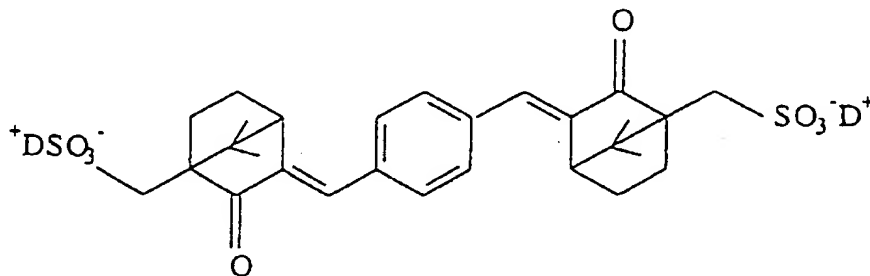
Another preferred dibenzoylmethane derivative according to the present invention is 4-isopropyldibenzoylmethane, sold under the name of "Eusolex[®] 8020" by Merck and corresponding to the following expanded formula:



The compounds of structures [sic] (IV) above are disclosed respectively in Patent US 4 585 597 and Patent Applications FR 2 236 515, 2 282 426, 2 645 148, 2 430 938 and 2 592 380.

5 A particularly preferred compound of formula (IV) is benzene-1,4-[di(3-methylidenecamphor-10-sulfonic acid)], such as the product sold under the name Mexoryl[®] SX by Chimex.

10 Benzene-1,4-[di(3-methylidenecamphor-10-sulfonic acid)] and its various salts (compound D), disclosed in particular in Patent Applications FR-A-2 528 420 and FR-A-2 639 347, are screening agents already known per se ("broad band" screening agents) capable in fact of absorbing ultraviolet rays with a wavelength ranging from 15 280 nm to 400 nm, with absorption maxima between 320 and 370 nm, in particular in the vicinity of 345 nm. These screening agents correspond to the following general formula:



20 in which D represents a hydrogen atom, an alkali metal or an $\text{NH}(\text{R}_{25})_3^+$ group, in which the R_{25} groups, which can be identical or different, represent a hydrogen atom or a $\text{C}_1\text{-C}_4$ alkyl or hydroxyalkyl group, or an M^{n+}/n group, M^{n+} representing a polyvalent metal cation in which n is

equal to 2 or 3 or 4, M^{n+} preferably representing a metal cation chosen from Ca^{2+} , Zn^{2+} , Mg^{2+} , Ba^{2+} , Al^{3+} and Zr^{4+} . It is clearly understood that the compounds of formula (IV) above can give rise to the "cis-trans" isomer about one or more double bond(s) and that all the isomers come within the scope of the present invention.

Mention may be made, as examples of specific benzimidazole or benzoxazole compounds corresponding to the formula (V), of:

- benzene-1,4-di(benzimidazol-2-yl-5-sulfonic acid),
- benzene-1,4-di(benzoxazol-2-yl-5-sulfonic acid), and their partially or completely neutralized forms.

Mention may more particularly be made, among benzophenone derivatives of formula (VI), of those chosen from the group composed of:

- 2,4-dihydroxybenzophenone (benzophenone-1), such as the product sold under the name Uvinul[®] 400 by BASF;
- 2,2',4,4'-tetrahydroxybenzophenone (benzophenone-2), such as the product sold under the name Uvinul[®] D50 by BASF;
- 2-hydroxy-4-methoxybenzophenone, also known as oxybenzone (benzophenone-3), such as the product sold under the name Uvinul[®] M40 by BASF;
- 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, also known as sulisobenzene (benzophenone-4), such as the product sold under the name Uvinul[®] MS40 by BASF; and its sodium sulfonate form (benzophenone-5);
- 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (benzophenone-6), such as the product sold under the name Helisorb[®] 11 by Norquay;
- 5-chloro-2-hydroxybenzophenone (benzophenone-7);
- 2,2'-dihydroxy-4-methoxybenzophenone, also known as dioxybenzone or benzophenone-8, such as the product sold under the name Spectrasorb[®] UV-24 by American Cyanamid;

- the disodium salt of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5,5'-disulfonic diacid or benzophenone-9, such as the product sold under the name Uvinul[®] DS49 by BASF;

5 - 2-hydroxy-4-methoxy-4'-methylbenzophenone (benzophenone-10);

- benzophenone-11, such as the product sold under the name Uvinul[®] M493 by BASF;

10 - 2-hydroxy-4-(octyloxy)benzophenone (benzophenone-12).

Mention may very particularly be made, among anthranilates which can be used according to the present invention, of menthyl anthranilate, such as the product sold under the name Neo Heliopan MA[®] by Haarman & Reimer.

15 The functionalized organic or silicone polymer of the material according to the invention can be a homopolymer or random, block and/or graft copolymer chosen from:

20 (a) alkyloxazoline homopolymers and copolymers, such as poly(2-ethyl-2-oxazoline);

(b) homopolymers and copolymers of (meth)acrylic acid, of crotonic acid, of maleic acid, of itaconic acid, of styrenesulfonic acid, of 2-(acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid and/or of vinylphosphonic acid;

25 (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, such as hydroxystyrene, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, such as fluorovinyl ethers, and
30 unsaturated organosilanes, organosiloxanes or
35 organopolysiloxanes;

- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, such as hydroxystyrene, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, such as fluorovinyl ethers, and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
- (f) polyethers, such as methylene oxide, ethylene oxide, propylene oxide or tetramethylene oxide homopolymers and copolymers;
- (g) aromatic and/or aliphatic polyesters, and polyesters obtained by ring opening, such as polycaprolactones, polylactides, polyglycolides and their copolymers;
- (h) homopolymers and copolymers of olefins or of cycloolefins, such as polyethylenes, ethylene/vinyl acetate, ethylene/ α -olefin, ethylene/cycloolefin or ethylene/(meth)acrylate copolymers, and propylene, butene, isobutene and norbornene homopolymers and copolymers;
- (i) polyamides, polyesteramides and polyetheramides;
- (j) optionally fluorinated polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;
- (k) fluoropolymers, such as the products sold by Ausimont under the name of "Fomblin[®]" (perfluoropolyether);
- (l) natural polymers and modified natural polymers, such as ether and/or ester derivatives of cellulose or of starch, polysaccharides, glycosaminoglucans and oligosaccharides, natural gums, such as hydroxyalkylated guar gums, such as those which are hydroxypropylated, hydroxypropylated guar gums

comprising carboxyl or quaternized functional groups, locust bean gum or xanthan gum, carrageenans, pectins, alginates, polypeptides or proteins, such as collagen, elastin, gelatin or keratin;

(m) polyorganosiloxanes, such as polydimethylsiloxanes, polymethylphenylsiloxanes or polyphenylsiloxanes, or polyorganosiloxanes substituted on the chain or at the chain end by amino acid groups, polyoxyethylene chains, amino or polyamino groups, hydroxyl groups, carboxylic acid groups, alkyl chains, vinyl or acrylic grafts or blocks, or fluorinated or perfluorinated grafts or blocks;

(n) polyorganophosphazenes;

(o) polysilanes, polycarbosilanes or polysilazanes; and

(p) mixtures of these polymers.

In a specific embodiment, the hydrocarbonaceous homopolymers and copolymers as mentioned above can possess polysiloxane chains as blocks and/or grafts.

The organic or silicone polymers can also comprise a cosmetically or dermatologically active group, such as those listed above.

In the case where organic or silicone polymers are not functionalized, they can be functionalized either by reaction within the actual composition, such as, for example, in the case of polyorganosiloxanes, or by prior reaction by conventional methods before the formation of the composition.

Mention may in particular be made, among preferred organic or silicone polymers according to the invention, of poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s, poly(vinyl alcohol [sic] and poly(vinylpyrrolidone). The most preferred are polydimethylsiloxane-diols.

When the material according to the invention comprises a precursor of the organic or silicone polymer, it is essentially one or more monomers capable of resulting in a functionalized organic or silicone polymer by polymerization of unsaturated double bonds or by polycondensation during application of the composition.

The polymerization can be initiated conventionally by a thermal route in the presence of conventional free radical initiators, by irradiation with UV radiation, by electron beams by the ionic route (cationic or anionic) or by any known polymerization technique.

Although this specific embodiment can be carried out according to the invention, it is nevertheless preferred, for practical reasons, to use a functionalized organic or silicone polymer which has already been formed.

The solvent used in the material of the present invention is preferably a linear or branched lower alcohol, better still ethanol.

The amounts of the various components of the material generally used are as follows, expressed with respect to the total weight of the material:

- from 0.1% by weight to 99% by weight, preferably from 0.5% by weight to 80% by weight and better still from 1% by weight to 70% by weight of metal alkoxide,
- from 0.1% by weight to 99% by weight, preferably from 0.5% by weight to 80% by weight and better still from 1% by weight to 70% by weight of functionalized organic or silicone polymer,
- from 0.1% by weight to 60% by weight, preferably from 0.1% by weight to 30% by weight and better still from 0.1% by weight to 20% by weight of sunscreen agent.

Another subject matter of the present invention relates to a process for shifting, into the range from 370 to 400 nm, the maximum absorption wavelength (λ_{max}) of

an organic UV-A screening agent having a λ_{\max} of less than 370 nm which consists in combining, with said screening agent, a sol comprising at least one functionalized organic polymer or one precursor of this polymer or at least one functionalized silicone polymer or one precursor of this polymer, at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides, at least one solvent and an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation. All the components are as defined above.

According to a preferred embodiment of the process of the invention, the metal alkoxide is mixed with a polymer solution before the addition of the screening agent.

An additional subject matter of the present invention is a cosmetic and/or dermatological composition comprising, in a cosmetically and/or dermatologically acceptable vehicle, a material as defined above according to the present invention.

This cosmetic and/or dermatological composition comprises the material according to the invention in an effective amount ranging from 1% by weight to 99% by weight, preferably from 5% by weight to 60% by weight, with respect to the total weight of the composition. The material according to the invention is preferably dried and milled and added in the form of particles to the composition. The mean size of the particles which are obtained after drying and milling lies within the range from 0.1 μm to 50 μm , preferably from 0.1 μm to 20 μm and better still from 0.1 μm to 10 μm .

The cosmetic and/or dermatological compositions targeted by the present invention can, of course, comprise one or more additional sunscreen agents other than the organic UV-A sunscreen agents defined above, these additional sunscreen agents being water-soluble,

fat-soluble or insoluble in the cosmetic solvents commonly used. These additional screening agents can be chosen in particular from cinnamic acid derivatives, salicylic derivatives, camphor derivatives other than those corresponding to the formula (IV), triazine derivatives, such as those disclosed in Patent Applications US-4 367 390, EP 0 863 145, EP 0 517 104, EP 0 570 838, EP 0 796 851, EP 0 775 698, EP 0 878 469, EP 0 933 376 and EP 0 893 119, β,β' -diphenylacrylate derivatives, benzimidazole derivatives, bisbenzoazolyl derivatives, such as those disclosed in Patents EP 0 669 323 and US 2 463 264; methylenebis(hydroxyphenylbenzotriazol) derivatives, such as those disclosed in Applications US-5 237 071, US-5 166 355, GB-2 303 549, DE-19 726 184 and EP 0 893 119, p-aminobenzoic acid derivatives, and the screening hydrocarbonaceous and screening silicone polymers disclosed in Application WO-93/04665.

Mention may be made, as examples of additional active sunscreen agents, of:

- p-aminobenzoic acid,
- ethoxylated (25 mol) p-aminobenzoate,
- 2-ethylhexyl p-dimethylaminobenzoate,
- N-propoxylated ethyl p-aminobenzoate,
- glyceryl p-aminobenzoate,
- homomenthyl salicylate,
- 2-ethylhexyl salicylate,
- triethanolamine salicylate,
- 4-isopropylbenzyl salicylate,
- 2-ethylhexyl 4-methoxycinnamate,
- methyl diisopropylcinnamate,
- isoamyl 4-methoxycinnamate,
- diethanolamine 4-methoxycinnamate,
- 2-ethylhexyl 2-cyano-3,3-diphenyl acrylate,
- ethyl 2-cyano-3,3-diphenyl acrylate,
- 3-(4'-methylbenzylidene)-d,l-camphor,

- 3-benzylidene-d,1-camphor,
- 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)-anilino]-1,3,5-triazine,
- 2-[(p-(tert-butylamido)anilino)-4,6-bis[(p-(2'-ethylhexyl-1'-oxycarbonyl)anilino)-1,3,5-triazine [sic],
- 2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine [sic] (Tinosorb[®] S, Ciba-Geigy),
- the polymer of N-(2- and 4-)[(2-oxoborn-3-yliden)methyl]benzyl]acrylamide [sic],
- 1,4-bis(benzimidazolyl)phenylene-3,3',5,5'-tetrasulfonic [sic] acid and its soluble salts,
- polyorganosiloxanes comprising a benzalmalonate functional group,
- polyorganosiloxanes comprising a benzotriazole functional group, such as drometrizole trisiloxane,
- 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol] in the dissolved form, such as the product sold under the trade name Mixxim[®] BB/100 by Fairmount Chemical, or else in the insoluble micronized form, such as the product sold under the trade name Tinosorb[®] M by Ciba-Geigy,
- 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(methyl)phenol] in the dissolved form, such as the product sold under the trade name Mixxim[®] BB/200 by Fairmount Chemical.

30 The cosmetic and/or dermatological compositions according to the invention can also comprise agents for the artificial tanning and/or browning of the skin (self-tanning agents), such as, for example, dihydroxyacetone (DHA).

35 The cosmetic and/or dermatological compositions according to the invention can also comprise pigments or

alternatively nanopigments (mean size of the primary particles: generally between 5 nm and 100 nm, preferably between 10 and 50 nm) formed of coated or uncoated metal oxides, such as, for example, nanopigments formed of titanium oxide (amorphous or crystalline titanium oxide in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide, which are all photoprotective agents well known per se which act by physical blocking (reflection and/or scattering) of UV radiation. Conventional coating agents are, furthermore, alumina and/or aluminum stearate. Such nanopigments formed of coated or uncoated metal oxides are disclosed in particular in Patent Applications EP-A-0 518 772 and EP-A-0 518 773.

The cosmetic and/or dermatological compositions in accordance with the present invention can additionally comprise conventional cosmetic adjuvants chosen in particular from fatty substances, organic solvents, ionic or nonionic thickeners, softeners, antioxidants, agents for combating free radicals, opacifiers, stabilizers, emollients, silicones, α -hydroxy acids, antifoaming agents, moisturizing agents, vitamins, fragrances, preservatives, surfactants, fillers, sequestering agents, polymers, propellants, basifying or acidifying agents, dyes or any other ingredient commonly used in the cosmetics and/or dermatological field, in particular for the manufacture of antisen compositions in the form of emulsions.

The fatty substances can be composed of an oil or a wax or their mixtures. The term "oil" is understood to mean a compound which is liquid at ambient temperature. The term "wax" is understood to mean a compound which is solid or substantially solid at ambient temperature and with a melting point generally of greater than 35°C.

Mention may be made, as oils, of mineral oils (liquid petrolatum); vegetable oils (sweet almond,

macadamia, blackcurrant seed or jojoba oil); synthetic oils, such as perhydrosqualene, fatty alcohols, acids or esters (such as the benzoate of C₁₂-C₁₅ alcohols sold under the name "Finsolv TN" by Finetex, octyl palmitate, 5 isopropyl lanolate or triglycerides, including those of capric/caprillic acids), or ethoxylated or propoxylated fatty esters and ethers; silicone oils (cyclomethicone, preferably comprising 4 or 5 silicon atoms, or polydimethylsiloxane); fluorinated oils; or 10 polyalkylenes.

Mention may be made, as waxy compounds, of paraffin wax, carnauba wax, beeswax or hydrogenated castor oil.

Mention may be made, among organic solvents, of 15 lower alcohols and polyols.

The thickeners can be chosen in particular from crosslinked polyacrylic acids, modified or unmodified guar and cellulose gums, such as hydroxypropylated guar gum, methylhydroxyethylcellulose or hydroxypropyl- 20 methylcellulose, and silicone gums, such as, for example, a polydimethylsiloxane derivative.

The cosmetic and/or dermatological compositions according to the invention can be prepared according to techniques well known to a person skilled in the art, in 25 particular those intended for the preparation of emulsions of oil-in-water or water-in-oil type.

This cosmetic and/or dermatological composition can be provided in particular in the form of a simple or complex emulsion (O/W, W/O, O/W/O or W/O/W), such as a 30 cream or a milk, or in the form of a gel or of a cream gel, of a powder or of a solid stick and can optionally be packaged as an aerosol and be provided in the form of a foam or of a spray.

The cosmetic and/or dermatological compositions 35 according to the invention are preferably provided in the form of an oil-in-water emulsion.

When it is an emulsion, the aqueous phase of the latter can comprise a nonionic vesicular dispersion prepared according to known processes (Bangham, Standish and Watkins, J. Mol. Biol., 13, 238 (1965), FR 2 315 991 and FR 2 416 008).

The cosmetic and/or dermatological composition according to the invention is used as composition for protecting the skin or keratinous substances against ultraviolet rays, as antisen composition or as makeup product.

When the cosmetic composition according to the invention is used for protecting the hair, it can be provided in the form of a shampoo, lotion, gel, emulsion or nonionic vesicular dispersion and can constitute, for example, a rinse-out composition, to be applied before or after shampooing, before or after dyeing or bleaching, or before, during or after perming or hair straightening, a styling or treating lotion or gel, a lotion or a gel for blow drying or hairsetting, or a composition for perming or straightening or for dyeing or bleaching the hair.

By way of indication, for antisen formulations in accordance with the invention which exhibit a vehicle of oil-in-water emulsion type, the aqueous phase (comprising in particular hydrophilic screening agents) generally represents from 50 to 95% by weight, preferably from 70 to 90% by weight, with respect to the entire formulation, the oily phase (comprising in particular lipophilic screening agents) from 5 to 50% by weight, preferably from 10 to 30% by weight, with respect to the entire formulation and the (co)emulsifier(s) from 0.5 to 20% by weight, preferably from 2 to 10% by weight, with respect to the entire formulation.

The examples are given by way of illustration of the present invention and are not understood in any way to be limiting.

Example 1

A material according to the invention is prepared from:

	Tetra-n-propyl zirconate	9.36 g
5	Absolute ethanol	2.83 g
	Polydimethylsiloxane-diol (PDMS-diol)	6.24 g
	Parsol [®] 1789	0.08 g
	Water	0.02 g

10 the tetra-n-propyl zirconate originating from Fluka, the Parsol[®] 1789 (4-tert-butyl-4'-methoxydibenzoylmethane) being sold by Hoffmann-Laroche and the PDMS-diol exhibiting a weight-average molar mass of 550 (ABCR, reference DMS-S12).

15 The PDMS-diol is diluted in ethanol. The tetra-n-propyl zirconate is subsequently added and the mixture is stirred for 5 minutes. The Parsol[®] 1789 is subsequently added with stirring. The novel material is ready for use.

20 Application and evaluation

The novel material is deposited on a glass sheet (microscope slide). A film is formed on the sheet after evaporation of the volatile components of the mixture. The drying time of the film is fast, that is to say
25 between 1 and 3 minutes.

The absorption band of the novel material is evaluated by UV visible absorption spectrometry. The λ_{\max} value has shifted to 378 nm with respect to the λ_{\max} of 358 nm of Parsol[®] 1789 before the preparation of the
30 material. The effectiveness of the novel material is not significantly reduced. This novel material is able to form a film, is entirely persistent toward water and ethanol and is not released under these conditions and in polar and nonpolar cosmetic oils.

Example 2

A material according to the invention is prepared from:

	Titanium tetraisopropoxide	2.27 g
5	Absolute ethanol	0.50 g
	Polydimethylsiloxane-diol (PDMS-diol)	0.40 g
	Parsol [®] 1789	1.10 g
	Tetrahydrofuran (THF)	2.25 g

10 the titanium tetraisopropoxide originating from Fluka, the Parsol[®] 1789 (4-tert-butyl-4'-methoxydibenzoylmethane) being sold by Hoffmann-Laroche, the PDMS-diol exhibiting a weight-average molar mass of 550 (ABCR, reference DMS-S12) and the tetrahydrofuran originating from Fluka.

15 The titanium tetraisopropoxide is diluted in ethanol. The Parsol[®] 1789, dissolved in the THF, is subsequently added to the solution with stirring over 20 minutes and then the PDMS-diol is added. The mixture is left to stir at ambient temperature for 60 minutes. The
20 novel material is then ready for use.

Application and evaluation

The application and evaluation are carried out in the same way as in Example 1. The λ_{\max} value was shifted
25 to 385 nm with respect to the λ_{\max} of 358 nm of Parsol[®] 1789 before the preparation of the material. The effectiveness of the novel material was not significantly reduced. This novel material is able to form a film, is
entirely persistent toward water and ethanol and is not
30 released under these conditions and in polar and nonpolar cosmetic oils.

Example 3

35 A material according to the invention is prepared from:

	Aluminum tri-sec-butoxide at 75% in sec-	
	butanol	0.36 g
	Polydimethylsiloxane-diol (PDMS-diol)	0.44 g
	Parsol [®] 1789	0.23 g
5	Tetrahydrofuran (THF)	2.25 g

the aluminum tri-sec-butoxide originating from ABCR, the
Parsol[®] 1789 (4-tert-butyl-4'-methoxydibenzoylmethane)
being sold by Hoffmann-Laroche, the PDMS-diol exhibiting
10 a weight-average molar mass of 550 (ABCR, reference DMS-
S12) and the tetrahydrofuran originating from Fluka.

The Parsol[®] 1789, dissolved in the THF, is added,
with stirring over 20 minutes, to the solution of
aluminum tri-sec-butoxide in sec-butanol and then the
15 PDMS-diol is added. The mixture is left to stir at
ambient temperature for 60 minutes. The novel material is
then ready for use.

Application and evaluation

20 The application and evaluation are carried out in
the same way as in Example 1. The λ_{\max} value was shifted
to 370 nm with respect to the λ_{\max} of 358 nm of Parsol[®]
1789 before the preparation of the material. The
effectiveness of the novel material was not significantly
25 reduced. This novel material is able to form a film, is
entirely persistent toward water and ethanol and is not
released under these conditions and in polar and nonpolar
cosmetic oils.